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Cavity ring-down spectrometer for high-fidelity molecular absorption measurements



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ABSTRACT

We present a cavity ring-down spectrometer which was developed for near-infrared measurements of laser absorption by atmospheric greenhouse gases. This system has several important attributes that make it possible to conduct broad spectral surveys and to determine line-by-line parameters with wide dynamic range, and high spectral resolution, sensitivity and accuracy. We demonstrate a noise-equivalent absorption coefficient of 4×10^{-12} cm⁻¹ Hz^{-1/2} and a signal-to-noise ratio of 1.5×10^6 :1 in an absorption spectrum of carbon monoxide. We also present high-resolution measurements of trace methane in air spanning more than 1.2 THz and having a frequency axing with an uncertainty less than 100 kHz. Finally, we discuss how this system enables stringent tests of advanced line shape models. To illustrate, we measured an air-broadened carbon dioxide transition over a wide pressure range and analyzed these data with a multispectrum fit of the partially correlated, quadratic speed-dependent Nelkin-Ghatak profile. We obtained a quality-of-fit parameter in the multispectrum fit equal to 36,000, thus quantifying small-but-measurable limitations of the model profile. This analysis showed that the line shape depends upon collisional narrowing, speed dependent effects and partial correlations between velocity- and phase-changing collisions.

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1. Introduction

Cavity ring-down spectroscopy (CRDS) is a powerful technique for accurate and sensitive measurements of atomic and molecular absorption spectra. As an alternative to more traditional Fourier-transform spectroscopy (FTS) measurements, it has many appealing attributes. These include insensitivity to external absorption and laser intensity noise, which can lead to nearly quantum-noise-limited detection limits, relatively long effective pathlengths associated with the high cavity finesse, and the potential for spectral resolution at the kHz level, when the probe laser frequency is commensurate with the linewidth of the ring-down cavity.

Originally developed with pulsed lasers [1], CRDS is now typically implemented using single-frequency, continuouswave (CW) lasers [2,3] which have frequency bandwidths that are much narrower than the characteristic mode spacing of the resonator. This approach results in decay signals that are closely approximated by a single exponential function. Thus ring-down spectra, which comprise an absorption signal superimposed on a cavity baseline, ideally can be determined directly from measured decay rates and frequency detuning of the probe laser. This property often makes CRDS the method of choice for the most demanding applications that require low measurement uncertainty and high sensitivity.

In the last decade, the use of fiber optics and solid-state sources such as external cavity diode lasers (ECDLs) and distributed-feedback (DFB) diode lasers has facilitated the use of CRDS in numerous laboratory, field and commercial applications. Lasers have been actively stabilized to ring-down



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cavities using the Pound–Drever–Hall (PDH) method [4,5], thus providing near-unity-efficiency transmission and pumping rates limited by the intrinsic build-up time of the cavity. Banks of near-ir DFBs have been configured to provide widely tuneable, single-frequency measurements of molecular absorption spectra which reveal hitherto unobserved weak spectral features for inclusion into modern spectroscopic databases [6], and which span wavelength regions encompassing entire molecular bands [7–10].

Length-stabilized ring-down cavities form the basis of the frequency-stabilized (FS)-CRDS technique [11-13] to provide an ultra-linear spectrum detuning axis for highprecision measurements of line shapes and spectroscopic parameters, yielding spectra with an exceptionally high signal-to-noise ratio (SNR) exceeding 2×10^5 [14], low limits of detection $(2 \times 10^{-12} \text{ cm}^{-1} \text{ in } 1 \text{ s averaging time})$ [15] and with absolute frequency axes linked via an optical frequency comb to a Cs clock [16]. A recently developed approach to CRDS, called frequency-agile rapid scanning spectroscopy (FARS) [15,17] overcomes the intrinsically slow thermo-mechanical tuning of DFB and ECDL probe lasers by incorporating high-bandwidth phase modulation methods driven by rapidly switchable microwave sources. Extremely high sensitivity $(5 \times 10^{-13} \text{ cm}^{-1} \text{ in } 1 \text{ s aver-}$ aging time) and wide dynamic range (6 decades) FS-CRDS has recently been demonstrated using a two-cavity configuration in which the probe laser is locked by optical feedback to an external cavity, with an extremely highfinesse (F=450,000) ring-down cavity being locked to the probe laser [18]. Taken together, a variety of CRDS spectrometers now compete with and surpass the performance of FTS instruments for the purposes of measuring relatively weak absorption transitions, especially in the visible and near-infrared regions.

Despite these substantial advances in CRDS, the particular realizations referred to above often suffer from tradeoffs between system robustness and simplicity, spectrum fidelity, mirror base losses, absorption dynamic range, wavelength coverage, spectrum sampling density, scanning speed, and both short-term and long-term measurement statistics. In the remainder of this paper, we present a relatively simple FS-CRDS spectrometer designed for routine, high-accuracy spectroscopic studies. To this end, we describe the unique elements comprising this system and present representative results that illustrate the system performance.

2. System overview

The principal goal of this study was to develop a ringdown spectrometer optimized for acquiring referencequality, room-temperature spectra of relevant atmospheric greenhouse gases (e.g., CO_2 , CO, H_2O , CH_4) in the nearinfrared region. Performance criteria included: robust and automated mode-to-mode scanning at rates up to 1 Hz over a wavelength range of tens of nanometers sufficient to capture entire rotation-vibration bands, signal acquisition rates comparable to a few times the inverse of the empty-cavity decay time with near-shot-noise limited measurement precision, an absolute spectrum frequency axis with an uncertainty of 100 kHz or less, cavity mode spacing sufficiently dense to adequately sample relatively narrow Doppler-broadened lineshapes at low pressures, and the ability to probe peak absorption losses of magnitude at least ten times the base cavity loss. Fig. 1 gives a schematic of the spectrometer, whose principal elements include a length-stabilized ring-down cavity containing two high-finesse mirrors, an I₂-stabilized and frequencydithered HeNe reference laser to which the ring-down cavity length is actively stabilized, a widely tuneable ECDL source amplified with a booster optical amplifier (BOA), a rapid-acquisition wavelength meter (WM) for laser locking and tuning, and a Cs-clock-referenced optical frequency comb (OFC) which provides an absolute wavelength reference.

2.1. Cavity construction and length stabilization

The ring-down cavity consists of an all-stainless-steel vacuum-compatible enclosure, within which resides a pair of spherical (1 m radius-of-curvature) mirrors. One cavity mirror is rigidly mounted and the other can be axially displaced over a 10 μ m range using a piezo-electric (PZT) assembly mounted external to the vacuum chamber. The mirror separation is approximately 139 cm, giving a freespectral-range (FSR) nominally equal to 108 MHz. The base mirror reflectivity at the probe laser wavelength is R=0.99998, corresponding to an empty-cavity finesse of 157,000 and linewidth of 0.64 kHz FWHM. The mirrors are also partially reflective (R=0.95) at a wavelength of 633 nm to enable active stabilization of the cavity length with respect to the reference HeNe laser. The cavity mirrors reside in adjustable flexure mounts each bolted to a right-angle plate resting on an optical table. Four invar rods (2.5 cm in diameter and 127 cm in length) connect the pair of angle plates to minimize



Fig. 1. Experimental setup. External cavity diode laser (ECDL); optical isolator (Iso); booster optical amplifier (BOA); wavelength meter (WM) with 10 MHz frequency resolution and 400 Hz update rate; Cs-clock-referenced, optical frequency comb (OFC); beat-note, fiber coupled (BN-FC) measurement; 8 MHz InGaAs, dc-coupled ring-down signal detector (Det₁); Si-PIN detector for HeNe reference laser (Det₂); variable-frequency acousto-optic modulator (AOM); dichroic mirror (DM); piezo-electric transducer for ring-down mirror actuation (PZT); 1₂ stabilized HeNe reference laser (HeNe) with 10 kHz long-term stability; proportional integral servo loop for cavity ECDL wavelength control (PI₁); PI loop for cavity length stabilization (PI₂).

the effects of thermal expansion. As described in Hodges et al. [11], length stabilization of the cavity is realized using an active locking scheme in which the 1f component of the transmitted HeNe light provides a discriminant signal. Here the reference laser frequency is modulated at 25 kHz using a fiber-coupled acousto-optic-modulator (AOM) with an optical modulation depth of 20 MHz. Phase-sensitive detection of the 1*f* component of the transmitted HeNe beam yields the error signal, which is fed back through a proportional-integral (PI) loop filter whose output forms the electronic feedback signal which actuates the ring-down cavity pzt to maintain transmission of the reference laser. This locking scheme makes the mirror-to-mirror distance impervious to room temperature variations, yielding a precision in the mode frequency (in the vicinity of 633 nm) at the 10 kHz level, limited by the longterm stability of the I2-stabilized HeNe reference laser. As described in Robichaud et al. [19], the length-stabilized cavity FSR can be found by measuring the optical frequency as the laser is sequentially stepped through longitudinal modes of the cavity. Using the OFC to measure the absolute laser frequencies, we scanned through approximately 14,000 resonances and measured an empty-cavity FSR of 108.750(2) MHz. Note that the exact FSR also can be determined at each sample pressure in order to compensate for dispersive effects in the refractive index of the gaseous cavity medium.

2.2. Probe laser locking

In order to probe absorption spectra, we use an ECDL which has a linewidth (50 ms average) of approximately 100 kHz. Achieving single-mode excitation of the ring-down cavity in FS-CRDS requires that we eliminate drift in the probe laser using an active feedback control scheme. Herein, we considered several strategies to achieve this goal. First, we maximized the rate of transmission bursts through the resonator (as described in Hodges and Ciuryło [12] and commonly implemented in most realizations of FS-CRDS) by slowly dithering the laser frequency about the cavity resonance. This method provides a robust laser locking scheme with an effective spectrum frequency resolution that is limited by the long-term stability of the ring-down cavity linewidth. In the present case, this stability is dictated by the performance of the reference HeNe laser. However, because of the low bandwidth of this servoing technique, the laser linewidth is not significantly narrowed on time scales corresponding to the cavity buildup time, and the maximum drift in the laser frequency is limited to approximately 1 MHz. Since laser spectral narrowing is not achieved, the average light throughput is relatively low because of the mismatch between the narrow ring-down cavity linewidth and the relatively broad laser linewidth. Rapid frequency variations in the laser thus lead to chaotic pumping of the cavity, with maximum signals that correspond to a mean transmission efficiency well below unity [20]. As discussed below, this technique also limits the precision with which the heterodyne beat frequency between optical frequency comb and the probe laser frequency can be determined.

As an alternative approach to stabilize the probe laser we considered implementation of the Pound–Drever Hall (PDH) locking method [21]. In the PDH method, optical sidebands are impressed upon the laser carrier frequency using a phase

modulator, and their heterodyne beat signal is monitored in reflection from a high-finesse cavity to produce a highbandwidth error signal for correcting the laser frequency. Because the PDH lock yields a relative linewidth of the laser that is narrow compared to the cavity resonance linewidth, light efficiently couples into the cavity to provide relatively high signal-to-noise ratios and minimal dead time between ring-down signal acquisitions. However, we have found that the PDH-locking strategy implemented in CRDS experiments is not without adverse consequences. In most PDH-locked CRDS approaches, a single beam polarization is used and the lock of the probe laser is interrupted each time a decay event is obtained [4,5,16]. Cygan et al. [22] found that with this single-beam, interrupted-lock approach, it is necessary to compensate for temperature-dependent drifts in the sideband-producing PDH phase modulator. Consequently, robustness and stability of this interrupted lock are difficult to achieve, with performance that tends to be system-specific. Moreover, the standard deviation of the cavity time constant measurements obtained with the PDH-locked case can be relatively large and far from the quantum noise limit [4,5]. In our recent FARS-CRDS experiment [15], we demonstrated that a dual-polarization scheme eliminated the need to interrupt the PDH lock, thus mitigating the problem of long-term lock stability. In that experiment, one polarization was continuous and dedicated to the PDH lock whereas the other yielded the periodically interrupted decay signal. This arrangement provided excellent lock stability and superb short-term measurement statistics, with fractional uncertainty in the ring-down time at the 8×10^{-5} level (about a factor of five above the quantum-noise-limited value), which we attribute to the high extinction ratio (80 dB) of the phase modulator switch [23]. However, we found that the long-term measurement statistics were compromised: an effect possibly caused by external cavities which affected the ring-down cavity base losses or polarization effects leading to birefringence and/or polarization-dependent losses in mirror reflectivity [24]. The recent dual-cavity FS-CRDS system described by Burkart et al. [18], which incorporated a PDH lock, yielded short-term measurement statistics exhibiting a longer minimum in the Allan deviation, which occurred at about 1 s.

In this study, we lock the probe laser using a rapid and precise WM that is operated in a closed-loop configuration $(PI_1 \text{ loop in Fig. 1})$ via the fine frequency tuning of the ECDL. As with the standard FS-CRDS probe laser lock described above, the detuning of the ECDL wavelength from the local ring-down mode is quantified by measuring the rate of transmission bursts through the ring-down cavity. First, the laser frequency is tuned through a TEM₀₀ cavity resonance such that the burst rate distribution about the WM frequency can be determined. We assign the WM frequency that maximizes the burst rate to be the local set point frequency. Second, the laser frequency is servoed using a proportional-integral (PI) algorithm acting as a loop filter, which produces an analog output that feeds back to the pztactuated fine-frequency control on the ECDL with a bandwidth of about 50 Hz. This servo minimizes the detuning relative to the set point frequency. This scheme gives an attractive alternative to the conventional frequency dithering/transmission burst method used in FS-CRDS (10 Hz bandwidth) because of its speed, and makes it possible to lock the excursions of the mean laser frequency to within approximately 100 kHz. We quantified this frequency stability by measuring fluctuations in the heterodyne beat frequency signal between the locked ECDL and our OFC and by measuring fluctuations in the WM-measured frequency when the laser was locked to the cavity. Although this method effectively eliminated drift in the mean laser frequency relative to the local cavity resonance, it had insufficient bandwidth to reduce the short-term laser linewidth to be commensurate with the ring-down cavity linewidth. In this regime, laser coupling into the cavity remains limited by rapid fluctuations in the laser frequency, as in the standard FS-CRDS dither lock. To augment the intensity of the transmitted signal, we used the BOA to produce incident powers of approximately 50 mW at the cavity input mirror. With transverse mode-matching efficiencies of approximately 90%, we achieved peak output signals of 3 uW, and ring-down repetition rates of up to 500 Hz. We note that this acquisition rate is within a factor of two of the maximum rate achievable using a PDH-locked system, assuming acquisition of decays lasting at least five empty-cavity time constants.

2.3. Measurement statistics

In CRDS, the absorption coefficient is determined in terms of variation in the measured decay time τ . For excitation of a single cavity mode, we model the time-dependent decay signal s(t) as

$$s(t) = s_0 \exp(-t/\tau(\nu_i)) + s_b,$$
 (1)

where τ is the intensity decay time at cavity mode frequency ν_j , s_0 is the decay signal amplitude and s_b is a constant offset. In this experiment each decay is digitized at 10 Msamples s⁻¹ with 16 bits of resolution, and the three parameters, (τ , s_0 , and s_b) are determined by unweighted least-squares fitting of Eq. (1) to the measured signals using the algorithm of Halmer et al. [25]. With $\tau(\nu_j)$ known, the loss spectrum is modeled by

$$\frac{1}{c\tau(\nu)} = \frac{L_0(\nu) + \Delta L_{et}(\nu)}{\ell} + \beta(\nu) + \alpha(\nu), \tag{2}$$

in which we have dropped the subscript *j* indicating the mode index, *c* is the speed of light, ℓ is the mirror-tomirror distance, $L_0 = 1 - \sqrt{R_1 R_2}$ is the mean mirror loss corresponding to intensity reflectivities of R_1 and R_2 , ΔL_{et} is an effective modulation in the mirror losses caused by coupled-cavity (i.e. etaloning) effects, and β and α are the scattering coefficient and absorption coefficient of the sample, respectively. Here the mirror loss, etaloning and scattering terms in Eq. (2) constitute the spectrum base-line and are accounted for using a sum of quadratic and sinusoidal functions that are consistent with the spectral dependence of the mirror reflectivity and Rayleigh scattering from the medium, and the observed periods, amplitudes and phases of residual etalons.

Assuming stationary behavior in the short-term measurement statistics, the standard deviation of the decay time σ_{τ} and the associated standard error $\sigma_{\tau}/k^{1/2}$ quantify the precision which is obtained over the time interval in which *k* ring-down measurements are acquired. For an average decay time $\overline{\tau}$, from

Eq. (2) it follows that the standard error in the measured absorption coefficient is $\Delta \alpha = \sigma_{\tau}/(c\bar{\tau}^2 k^{1/2})$. Introducing the ring-down decay acquisition rate $f_a = k/\Delta t$, then we can define the noise-equivalent-absorption coefficient NEA (units of cm⁻¹ Hz^{-1/2}) as the standard error $\Delta \alpha$, obtained over an averaging time $\Delta t = 1$ s. This definition reduces to

$$NEA = \frac{\sigma_{\tau}}{c\bar{\tau}^2 \sqrt{f_a}}$$
(3)

More generally, stationary (hence ergodic) statistical behavior cannot be achieved for indefinite time intervals, making it useful to replace $\sigma_{\tau}/k^{1/2}$ by the Allan deviation $\sigma_{\tau A}$ [26,5]. This approach accounts for non-statistical measurement drift and gives an upper bound to the time interval over which the system is statistically stationary. Two measured Allan deviations are shown as a function of the averaging bin number kin Fig. 2. These sets of data correspond to 1) the empty-cavity case (base loss of 1.4×10^{-7} cm⁻¹), and to 2) the laser tuned to the peak of a molecular transition (absorption losses $3.3 \times$ base loss). The NEA for the empty-cavity case is $4.2 \times$ 10^{-12} m⁻¹ Hz^{-1/2}, with the minimum detectable absorption coefficient α_{min} of 1.5×10^{-12} cm⁻¹ occurring on an averaging time scale of ≈ 10 s. The Allan deviation for the absorbing case is qualitatively similar to the empty-cavity case but has a slightly longer averaging time minimum. Because the two cases have nearly the same relative standard deviation in their decay times, the Allan deviation results for the absorbing case are shifted vertically relative to those of the empty-cavity case by the ratio of the total losses.

Table 1 of Long et al. [15] compares reported NEA values for various cavity-enhanced spectroscopic methods, including noise-immune cavity-enhanced optical heterodyne molecular spectroscopy (NICE-OHMS) [27], CRDS [28], and FARS-CRDS. As discussed therein, the FARS-CRDS method, with a demonstrated NEA of 1.7×10^{-12} cm⁻¹ Hz^{-1/2} gives the lowest NEA reported for a spectrometer with a wavelength tuning range > 0.2 nm. The present system gives a NEA nearly halfway between the FARS-CRDS value



Fig. 2. Allan deviations vs. averaging bin number *k*, for empty cavity conditions (bottom trace) and with the probe laser locked to the cavity at the peak of the air-broadened (30012) ← (00001) R16e band ¹²C¹⁶O₂ transition at $\tilde{\nu} = 6359.9673 \text{ cm}^{-1}$ (upper trace). The latter case corresponds to a CO₂ molar fraction of 345 µmol mol⁻¹ at *p* = 40 kPa and room temperature, which gives a peak single-pass absorption coefficient of $6.2 \times 10^{-7} \text{ cm}^{-1}$. The indicated NEA for the empty cavity is based on a relative standard uncertainty in τ of 0.04% and a ring-down acquisition rate of 310 Hz.

of Long et al. $(2.5 \times \text{greater})$ and that of the widely tunable (200 nm) PDH-locked CRDS system reported by Martínez et al. [4] ($3.5 \times \text{lower}$). Although not previously reported, α_{min} for the FARS-CRDS of Long et al. [15] is ten times greater than the present case because of the relatively short time interval (13 ms) during which the measurement statistics were stationary. We also note that a detection limit of $1.4 \times 10^{-13} \text{ cm}^{-1}$ in a 4 s averaging time was recently demonstrated by Burkart et al. [18] using a dual-cavity scheme that incorporated optical feedback for laser locking.

3. Spectroscopic measurements

3.1. Survey spectra of methane in air

In order to illustrate the sensitivity and spectral fidelity of our system, we measured room-temperature spectra of a NIST-certified air mixture containing trace quantities of methane and carbon dioxide. A representative result covering a 40 cm⁻¹-wide region about 6160 cm⁻¹ at 13.3 kPa is shown in Fig. 3. Here the baseline cavity ring-down spectrum obtained under empty-cavity (vacuum) conditions was subtracted from the measurements. The calculated spectrum of methane for the known molar fraction $(11.8376 \,\mu\text{mol mol}^{-1} \pm 0.0039 \,\mu\text{mol mol}^{-1})$ is also shown in Fig. 3 as well as the carbon dioxide spectrum assuming a molar fraction of nominally 400 μ mol mol⁻¹. Both calculated spectra are based upon the respective HITRAN 2012 [29] line lists, where the methane line list in this region corresponds to Campargue et al. [30]. The frequency axis was calibrated on an absolute basis by measuring the heterodyne beat frequency between the locked probe laser and the OFC at nominally 15 positions along the x-axis. Comparison of these data at the scale of Fig. 3 suggests exceptional agreement between the measurements and calculated values. However, upon closer inspection as illustrated in Fig. 4, statistically significant differences between the measured and calculated methane absorption spectra



Fig. 3. Bottom: measured survey spectrum of methane-in-air mixture for p=13.3 kPa, T=296 K and methane molar fraction of 11.8376 ± 0.0039 µmol mol⁻¹. Middle and Top: modeled spectra for CH₄ and CO₂ based on the HITRAN 2012 line list. The baseline is subtracted from the measured spectrum, and the two calculated spectra are vertically shifted for clarity.

are evident. The calculated integrated absorbance over the wave number range 6135–6155 cm⁻¹ was about 2% low of the measured value. Closer inspection of the individual methane transitions (not shown) reveals peak location differences as large as 30 MHz between the calculated and observed values. We assign these differences to uncertainties in the methane line list transition frequencies. We verified the accuracy of our frequency axis by measuring the R6e (300013) \leftarrow (00001) ¹²C¹⁶O₂ transition over the pressure range 1.33–13.3 kPa. We obtained a zero-pressure transition frequency of 186,866,121.194(074) MHz, in good agreement with the literature value of 186,866,121.122(8) MHz [31]. We also obtained a pressure-shifting parameter coefficient of δ = – 1.283(11) MHz kPa⁻¹ which is within 0.3% of the HITRAN 2012 [29] δ value for this transition.

3.2. Spectra with high signal-to-noise ratio

Because line parameters are generally obtained by fitting theoretical line profiles to measured absorption spectra, the ability to distinguish between blended transitions and to resolve differences in the fidelity of fitted profiles depends upon the spectrum SNR. We note that the SNR, which we define as the ratio of the peak absorption to the root-mean-square deviation in the baseline, is a measure of the dynamic range of the spectrometer.

In order to quantify the spectrum SNR and its dependence on averaging time, we made repeated measurements of an isolated transition of carbon monoxide (CO). Each spectrum was acquired in 5 min and spanned a 6 GHz-wide frequency window. We found that individual spectra had SNR values of \approx 440,000:1. Averaging *N* spectra gave a SNR that increased ergodically (\sqrt{N} dependence) up to *N*=8 (corresponding to an averaging time of 40 min). For larger *N* and longer averaging times, however the SNR increased more slowly and was nominally proportional to *N*^{0.3} up to *N*=68. We attribute the non-stationary behavior at long time scales, to slowly varying etalons driven by temperature and pressure drift in the laboratory. See Courtois et al. [32] for a description of how drift in



Fig. 4. Zoom of air-broadened methane survey spectrum shown in Fig. 3. Measurements (symbols), CH_4 model (blue line), CO_2 model (shifted red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 5. High signal-to-noise ratio (SNR) absorption spectrum of the *P*8 ($3 \leftarrow 0$)¹²C¹⁶O transition at 6316.7509 cm⁻¹. Symbols: average of 68 spectra acquired in 5.6 h. Line: least-squares fit of the speed-dependent Nelkin-Ghatak profile to the measured spectrum. The sample was 2.5 mmol mol⁻¹ of CO in N₂ at *p*=10.7 kPa. The indicated SNR is based on the ratio of peak absorption ($\alpha = 3.3 \times 10^{-6}$ cm⁻¹) to the standard deviation of the baseline in the fit residuals.

laboratory temperature and ambient pressure influence the base losses of a length-stabilized ring-down cavity. Fig. 5 shows the average of 68 spectra (symbols) along with a least squares fit (line) of the quadratic speed dependent Nelkin-Ghatak profile (gSDNGP) described below. The fit residuals (obs. - calc.) are given in the lower panel and reveal systematic deviations (at the 1 part in 7000 level) in the spectrum not captured by the SDNGP. However, we find a SNR of 1.5×10^6 :1, which to our knowledge is the highest SNR ever reported in a laser spectroscopic measurement, surpassing the previously reported SNRs of 700,000:1 [18], 220,000:1 [14] and 170,000:1 [32], all of which were obtained with FS-CRDS systems. The only other absorption method yielding SNRs of similar-magnitude is the chirped-pulse Fourier-transform spectroscopy (CP-FTS) technique, which has been demonstrated in the microwave (SNR $\approx 200,000$) [33] and terahertz (SNR \approx 100,000) [34] regions.

3.3. Advanced line shape models

For spectra with SNRs less than about 500, the Voigt profile (VP) typically provides adequate representation of molecular line shapes, because deviations from the VP are generally below the spectrum baseline noise level. Nevertheless, although most spectroscopic databases of atmospheric molecules assume the VP for line shape, it is well known that the VP often does not adequately capture the pressure-dependence and temperature-dependence of spectra acquired at high SNR. Specifically, studies of non-Voigt line shapes which address phenomena such as collisional (Dicke) narrowing and speed dependent effects require measured spectra with SNRs of the order of a few thousand. This level of spectroscopic measurement quality was first demonstrated nearly two decades ago using laser-based methods, yielding quantitative information characterizing the physics of atomic and molecular line shapes [35–37]. More recently, spectra based on direct absorption of single-frequency lasers have given SNRs of 10,000 or more. These improvements were driven by the use of precise frequency references and intensity stabilization methods [38]. As mentioned above, much higher SNRs have been reported using the FS-CRDS method (also see for example Long et al. [39]) which is relatively immune to amplitude and frequency noise in the source laser. This level of spectroscopic precision opens up an entirely new domain where exceedingly stringent tests of advanced line shape theories can be put to the test. Recently, Wcisło, et al. [40] discussed how advanced line shape profiles that incorporate speed-dependent effects and velocitychanging collisions (calculated assuming various interaction potentials) can vield quality-of-fit parameters (defined below) of approximately 90.000 when fit to the high-SNR data of Cygan et al. [14], therefore illustrating how progress in the theory of line shapes can be driven by advanced measurements.

There are numerous alternative profiles which account for higher-order non-Voigt effects. Of these, the partially correlated, quadratic speed-dependent hard-collision profile (pCqSDHCP) has been selected to be an appropriate line shape model for incorporation into spectroscopic databases [41,42]. This profile can be calculated in terms of the VP and contains additional parameters accounting for collisional narrowing effects, speed dependence of broadening and shifting, and effects of partial correlation between velocity- and phase-changing collisions. As discussed in Sironneau and Hodges [43], the pCqSDHCP is equivalent to the partially correlated, quadratic speeddependent, Nelkin–Ghatak profile (pCqSDNGP) used here and which we present next for completeness.

We begin by defining the reduced absorber speed $x = v/v_p$, where v_p is the most probable speed, $u = (\omega - \omega_0)/\omega_D$ is the reduced angular frequency detuning about line center ω_0 , and ω_D is the 1/*e* Doppler width, With these definitions, we can write the complex speed-dependent Voigt profile (SDVP) as [44]

$$\tilde{I}_{SDV} = \frac{2}{\pi^{3/2}} \int_{-\infty}^{\infty} dx \, e^{-x^2} x \left\{ \tan^{-1} \left[f(u,x) \right] + \frac{i}{2} \ln \left(1 + f(u,x)^2 \right) \right\}$$
(4)

in which *g* and *d* are the mean collisional relaxation rate Γ_0 , and the mean collisional shift Δ_0 , normalized by ω_D , respectively, and $f(u, x) = [u - dB_s(x) + x]/[gB_w(x)]$. Assuming a quadratic speed dependence for the collisional broadening and collisional shifting gives $B_w(x) = 1 + a_w(x^2 - 3/2)$ and $B_s(x) = 1 + a_s(x^2 - 3/2)$, respectively. Here the empirical terms a_w and a_s are the broadening speed dependence parameter, respectively. With these substitutions, the pCqSDNGP can be written as [45]

$$I_{pCqSDNG} = \operatorname{Re}\left\{\frac{\tilde{I}_{qSDV}^{*}(u;gB_{w}+Z)}{1 - \pi z \tilde{I}_{qSDV}^{*}(u;gB_{w}+Z))}\right\}$$
(5)

where $\tilde{I}_{SDV}^{*}(u)$ is the function $\tilde{I}_{SDV}(u)$ with $gB_{w}(x)+z$ substituted for $B_{w}(x)$. The term $z = \omega_{opt}/\omega_{D}$, where ω_{opt} is the optical angular frequency of velocity-changing collisions,

accounts for narrowing of the line profile. Generalizing *z* to be a complex quantity accounts for the influence of partial correlation between velocity- and phase-changing collisions on line narrowing. With this generalization, $\omega_{\rm opt}$ can be written in terms of the mean collisional relaxation rate Γ_0 and mean collisional shift of line center Δ_0 as

$$\omega_{\text{opt}} = \omega_{\text{eff}} - \eta_{\Gamma} \Gamma_0 + i \eta_{\Lambda} \Delta_0 = \text{Re}\{\omega_{\text{opt}}\} + \text{Im}\{\omega_{\text{opt}}\},\tag{6}$$

where η_{Γ} and η_{Δ} are semi-empirical correlation parameters and $\omega_{eff} = k_B T / (m_a D)$ is the effective frequency of velocitychanging collisions associated with the mass diffusion coefficient *D* of the absorber of mass m_a in the buffer gas at temperature *T*. Note that the pCqSDNGP reduces to the VP, Nelkin–Ghatak profile (NGP), quadratic speed-dependent Voigt profile (qSDVP) and quadratic speed-dependent Nelkin–Ghatak profile (qSDNGP) for Im { ω_{opt} } = 0 when ($a_w, a_s, \text{Re}\{\omega_{opt}\} = (0, 0, 0), (a_w, a_s) = (0, 0), (\text{Re}\{\omega_{opt}\} = 0)$ and (Re{ ω_{opt} } = ω_{eff}), respectively.

3.4. Measurements of carbon dioxide line shape parameters

In climate studies, the remote sensing of carbon in the atmosphere typically involves measuring and modeling the transmittance of solar radiation by carbon dioxide. Important examples include the GOSAT [46] and Orbiting Carbon Observatory 2 (OCO-2) [47] satellites, as well as ground-based FTS measurements within the Total Carbon Column Observing Network (TCCON) [48]. All of these studies require accurate line parameters to enable the determination of carbon dioxide concentration with relative uncertainties at sub-percent levels. To support this effort, we are investigating line shape effects in the near-infrared bands of carbon dioxide near 1.6 μ m.

In Fig. 6 we present a series of 7 spectra of the (30012) \leftarrow (00001) R16 $^{12}C^{16}O_2$ transition at 6359.9673 cm⁻¹. These spectra were acquired over the pressure range 1.33–26.7 kPa on air-broadened samples of carbon dioxide (427 nmol mol⁻¹) in Ar-free, synthetic air. This pressure range corresponds to Lorentzian-to-Doppler width ratios between 0.16 and 3.3. The average gas temperature was

296.215 K, with a standard deviation of 22 mK. Changes in sample temperature were driven primarily by variations in the laboratory temperature. For the gas pressure measurements, we estimate the average standard relative uncertainty to be 4×10^{-5} . We modeled the pressure-dependent evolution of these measured spectra using the pCqSDNGP, and we carried out a multispectrum fit of the spectra acquired at all pressures where all fitted data points were equally weighted. We constrained the fitted parameters Γ_0 , Δ_0 , Re{ ν_{opt} }, and Im{ ν_{opt} } to be proportional to pressure *p*, we floated the peak areas A and line centers ν_0 , and we assumed a_w and a_s were independent of pressure. It was also necessary to model an interfering transition at 6360.11309 cm⁻¹ $({}^{12}C^{16}O_2 \text{ R4} (31112) \leftarrow (01101))$, which we calculated as a NGP with a variable narrowing width. The spectrum model also accounted for five weaker carbon dioxide interferences. which were modeled by the VP using calculated collisional widths based on the HITRAN 2012 air-broadening coefficients. The positions and areas of these weak transitions were treated as fitted parameters. Other fitted parameters included the baseline and slope for each spectrum, and a single etalon (measured in the empty-cavity case) and having a frequency of approximately 25 GHz. We assigned this etalon to coupledcavity effects within the ring-down cavity mirrors.

The results (spectra and fit residuals) of the multispectrum study are given in Fig. 6. Above each residual spectrum in Fig. 6 we note the quality-of-fit parameter (QF), defined by Cygan et al. [14] as

$$QF = \frac{(\alpha_{max} - \alpha_{min})}{\widetilde{S}_R},\tag{7}$$

in which \widetilde{S}_R is the standard deviation of the fit residuals equal to

$$\widetilde{S}_{R} = \sqrt{\frac{\sum_{i=1}^{M} \alpha_{exp}(\nu_{i}) - \alpha_{fit}(\nu_{i})^{2}}{M - k_{p}}},$$
(8)

where α_{exp} and α_{fit} are the measured and fitted absorption coefficients, respectively, ν_i is the *i*th frequency in the



Fig. 6. Top panel: absorption spectra of the R16 (30012) \leftarrow (00001) $^{12}C^{16}O_2$ transition for the indicated pressures. Bottom panel: corresponding fit residuals and quality of fit (QF) parameters based on a multi-spectrum fit of the pCqSDNGP to the measured spectra. The gas sample consisted of 427 nmol mol⁻¹ of carbon dioxide in synthetic, Ar-free air.

measured spectrum, M is the number of measured spectrum points and $k_{\rm p}$ is the number of adjustable parameters in the multispectrum fit. The composite QF for the multispectrum fit is 36,129. For all but the lowest pressure case where QF = 11,019, we obtain QF for each spectrum ranging from 21,402 to 30,878 (at p=20 kPa). The QF is lower than the SNR based on the baseline residuals primarily because of relatively large systematic residuals in the core of the line. For single-spectrum fits at fixed pressure (not shown), we obtain QF values of approximately 70,000, although the results yield less physically reliable values for a_w and ω_{opt} than those obtained from the multispectrum fit, because of correlation between these fitted parameters. Using numerical simulations of spectra, we also investigated the extent to which nonlinearity in the measurement of sample pressure and temperature could account for the observed systematic residuals in our multispectrum fit. We find that given the low uncertainty of our pressure and temperature measurements, the observed systematic residuals cannot be assigned to uncertainties in the measurement of these quantities. The decay signals also exhibit some small systematic departures (at the one part per several thousand level) from exponential behavior, which we attribute to the high-speed board used to digitize the signals. However, given the constant trigger level for all acquired spectra and the relatively small range of peak losses, this effect should introduce only a constant offset to the base losses. This leads us to assign the non-zero residuals in the line core to limitations of the pCqSDNGP model to capture the pressure dependence of the observed line shape.

As an illustration of the precision and accuracy with which line positions can be determined using the present technique, we present results based on six air-broadened spectra acquired over the pressure range 0.67–20 kPa using the same gas sample and transition as discussed in Fig. 6. In this analysis, we did single spectrum fits in which only the line center position and spectrum area were



Fig. 7. Top panel: measured line centers (relative to ν_{ref} = 190,666,990 MHz) for the air-broadened R16 (30012) \leftarrow (00001) $^{12}C^{16}O_2$ transition at the indicated pressures. Bottom panel: corresponding fit residuals for the linear regression of ν with measured *p*. The sample gas is the same as in Fig. 6.

floated, with the other line parameters constrained to the values obtained in the multispectrum fit given above. The results, which are summarized in Fig. 7, yield the zeropressure position ν_0 , and air-broadened, pressure-shifting coefficient δ for this transition. The average standard uncertainty in the fitted position was 60 kHz, and the standard deviation of the fit residuals resulting from the linear regression of ν_0 with p, has a standard deviation of 37 kHz, thus illustrating excellent measurement linearity. To evaluate systematic sensitivity of ν_0 and δ to the pCqSDNGP parameters, we also measured line centers by additionally floating a_w , a_s , Re{ ν_{opt} } and Im{ ν_{opt} }. This reanalysis changed ν_0 by 120 kHz and δ by 0.3%. Adding the frequency uncertainties in quadrature with an estimated 100 kHz uncertainty in the lock-point gives a combined standard uncertainty of 167 kHz for ν_0 . The present measurement of $\nu_0 = 190,667,021.673$ is in good agreement ($\delta \nu_0 = 265 \text{ kHz}$) with our recent unpublished result (190,667,021.408(40) MHz) obtained using an OFCcomb-referenced, PDH-locked FARS-CRDS experiment [16] but is more than 2 MHz less than the HITRAN 2012 value. For δ , we find that our measurement differs in magnitude from the HITRAN 2012 value by 4.6%, which is statistically significant given that $u_r(\delta)$ is 0.35%.

All of the fitted line parameters and uncertainties for the R16 ¹²C¹⁶O₂ transition are summarized in Table 1. The pressure broadening coefficient (given by $\gamma = \Gamma_0/(2\pi p)$ and temperature corrected to T=296 K) has a relative uncertainty of about 0.1% and is 0.5% lower than the corresponding HITRAN 2012 value. Multispectrum fitting of the qSDNGP to FS-CRDS measurements of the same carbon dioxide transition were reported by Long et al. [49], where correlation effects were not considered because of limited measurement precision. This prior study showed that both collisional narrowing and speed-dependence effects influence the line shape, which is a result confirmed here. However, we find that correlation between

Table 1

Results of pCqSDNGP multispectrum fit to the measured (30012) \leftarrow (00001) R16⁻¹²C¹⁶O₂ transition. All quantities (except for a_{wr} , a_s and η_T which are dimensionless) are in units of kHz Pa⁻¹ and specified at 296 K. We calculate the pressure broadening and pressure shifting coefficients as $\gamma = \Gamma_0/(2\pi p)$ and $\delta = \Delta_0/(2\pi p)$ respectively. The correlation parameter η_T is given by $(\omega_{diff}/(2\pi p) - \text{Re}(\omega_{opt})/(2\pi p))/\gamma$. The specified relative uncertainties are standard deviation and based on the fit statistics and estimated systematic errors. For comparison, we show the pressure broadening coefficient γ_{HT} and pressure shifting coefficient δ_{HT} from HITRAN 2012 as well as the calculated value for the narrowing frequency per-unit-pressure $\omega_{diff}/(2\pi p) = k_B T/(2\pi m_a pD)$. This latter quantity is based on the mass diffusion coefficient of CO₂ in air D=0.159 cm² s⁻¹ at (296 K, 101 kPa), taken from Fig. 3 of Ref. [50]. The factor 1 cm⁻¹ atm⁻¹ = 295.872 kHz Pa⁻¹ can be used to convert the values into conventional units.

Lineshape parameter	Value	Rel. unc. (%)
a_w a_s γ δ $\operatorname{Re}\{\omega_{opt}\}/(2\pi p)$ η_{Γ} γ_{HT} δ_{HT} $\omega_{diff}/(2\pi p)$	$\begin{array}{c} 0.0883\\ 0.0557\\ 22.048\\ -1.566\\ 0.926\\ 0.208\\ 22.161\\ -1.497\\ 5.50\\ \end{array}$	0.2 20 0.1 0.35 1 1

the velocity-changing and dephasing collisions also must be included in modeling the evolution of the line shape with pressure. Our pCqSDNGP fit gives $\text{Re}\{\omega_{ont}\}/\omega_{diff} =$ 0.17 \ll 1 and $\eta_{\Gamma} = 0.209$ which is indicative of a large reduction in collisional narrowing. Likewise, fitting the qSDNGP to the present spectra yields a ω_{opt} (in this case a real quantity) which is similar to the pCqSDNGP result. A concurrent FS-CRDS line shape study of the (20013) \leftarrow (00001) R24 and R30 ¹²CO² transitions gave similar results, where pCqSDNGP fits gave $\eta_{\Gamma} \approx 0.22$ [51]. Given the uncertainty in the determination of a_s (20%), the present measurement is consistent with that previously reported in [49]. Moreover, we find that setting a_s to zero clearly degrades the fit quality, indicating that the speeddependent shifting has a measurable effect on the line shape. In contrast, we found that the fitted value of $Im\{\omega_{ont}\}$ (not reported in Table 1) was dependent on the initial guess in the least-squares fit, making this quantity indeterminate.

4. Conclusions

We have presented a cavity ring-down apparatus that was designed to provide accurate spectroscopic measurements of greenhouse gases such as carbon dioxide, methane, carbon monoxide and water vapor. With the addition of a similar laser to extend the spectral coverage, the spectrometer covers the wavelength range 1570 nm to 1670 nm, providing a dynamic range in absorption exceeding 10⁶, a standard uncertainty in frequency nominally equal to 100 kHz, a noise-equivalent absorption coefficient of 4×10^{-12} cm⁻¹ Hz^{-1/2} and decay signal acquisition rate of up to 500 Hz. Its high level of performance was enabled by the use of high-reflectivity mirrors (1-R) 2×10^{-5}), a relatively long (1.4 m) resonator with active length stabilization (i.e., frequency-stabilized CRDS method), and a widely tunable, single-frequency ECDL amplified to emit tens of mW of power and actively frequency locked to the resonator using a fast, highprecision wavelength meter. Because the described system was assembled by integrating commercially available technology, we emphasize that similar FS-CRDS spectrometers operating in the visible and near-infrared spectral regions could readily be built with this approach. We expect that the combination of sensitivity, accuracy, tuning speed and spectral coverage which is afforded here will enable increasingly stringent tests of theoretical frequencies, intensities and shapes of molecular spectra.

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